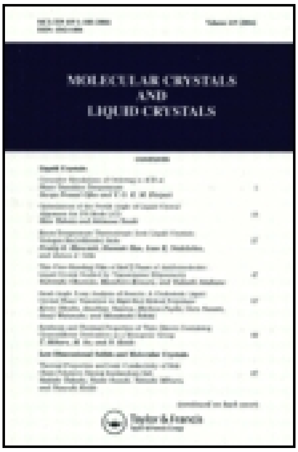

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Reversible, Metastable, Ultrafast Photoinduced Electron Transfer in Conjugated Polymer and Buckminsterfullerene Composites and Heterojunctions

N. Serdar Sariciftci [a] & Alan J. Heeger [a]

[a] Institute for Polymers & Organic Solids, University of California, Santa Barbara, California, 93106, USA

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REVERSIBLE, METASTABLE, ULTRAFAST PHOTOINDUCED ELECTRON TRANSFER IN CONJUGATED POLYMER AND BUCKMINSTERFULLERENE COMPOSITES AND HETEROJUNCTIONS

N. Serdar SARICIFTCI and Alan J. HEEGER
Institute for Polymers & Organic Solids, University of California,
Santa Barbara, California 93106, USA

Abstract Results of comparative, experimental studies on the reversible, metastable, ultrafast photoinduced electron transfer from semiconducting, conjugated polymers onto C_{60} are summarized. Photoinduced absorption in millisecond and femtosecond time scales, steady state and picosecond time-resolved photoluminescence, steady state and picosecond transient photoconductivity, steady state infrared photoexcitation spectroscopy and finally steady state light induced electron spin resonance measurements are summarized as experimental evidence for an ultrafast (< 1 picosecond) forward electron transfer resulting in a long-lived charge separated state. Comparative studies demonstrate that in degenerate ground state polymers soliton excitations, and in polydiacetylenes the strongly bound excitons, form before the electron transfer occurs; thereby inhibiting charge separation. Utilizing thin films of the semiconducting polymer and buckminsterfullerene to form a heterojunction interface, we have fabricated donor-acceptor diode bilayers which functioned as photodiodes and photovoltaic cells.

INTRODUCTION

The parallel interests of understanding natural photosynthesis in biological systems and of efficiently harvesting solar energy as an alternative to fossil fuels have led to a substantial, multidisciplinary effort in the field of photoinduced electron transfer phenomena in physics, chemistry, biology and in their regimes of overlap [1]. A basic description of intramolecular and/or intermolecular photoinduced electron transfer is as follows:

Step 1: $D + A \rightarrow {}^{1,3}D^* + A$, (excitation on D);
Step 2: ${}^{1,3}D^* + A \rightarrow {}^{1,3}(D -- A)^*$, (excitation delocalized on D-A complex);
Step 3: ${}^{1,3}(D -- A)^* \rightarrow {}^{1,3}(D^{\delta+} -- A^{\delta-})^*$, (charge transfer initiated);
Step 4: ${}^{1,3}(D^{\delta+} -- A^{\delta-})^* \rightarrow {}^{1,3}(D^{+\bullet} -- A^{-\bullet})$, (ion radical pair formed);
Step 5: ${}^{1,3}(D^{+\bullet} -- A^{-\bullet}) \rightarrow D^{+\bullet} + A^{-\bullet}$, (charge separation);

where the donor (D) and acceptor (A) units are either covalently bound (intramolecular), or spatially close but not covalently bonded (intermolecular); 1 and 3 denote singlet or triplet excited states, respectively. The partial charge transfer at Step 3 is strongly dependent on effects of the surrounding medium, such as the polarity of the solvent *etc.* resulting in a continous range for the transfer rate $0<\delta<1$. At Step 4, if $\delta=1$, a whole electron is transferred. At each step, the D-A system can relax back to the ground state either by releasing energy to the "lattice" (in the form of heat) or through light emission (provided the radiative transition is allowed). Permanent changes that might occur from ion radical reactions beyond step 5 are not considered here, even though their importance in photochemical and photoelectrochemical reactions has been established. The electron transfer (step 4) describes the formation of an ion radical pair; this does not occur unless $I_{D*} - A_A - U_C < 0$, where I_{D*} is the ionization potential of the excited state (D*) of the donor, A_A is the electron affinity of the acceptor, and U_C is the Coulomb energy of the separated radicals (including polarization effects). Stabilization of the charge separation (step 5) can possibly be enabled by carrier delocalization on the D^+ (and/or A^-) species and by structural relaxation.

Light harvesting polymer systems utilizing photoinduced energy and/or electron transfer mechanisms are attracting more and more attention within the scientific community [2]. Polymers are particularly interesting in this field of photophysics/photochemistry because new synthetic methods (as developed through polymer chemistry and material science) make it possible to modify, functionalize and derivatize donor and acceptor units.

Recently, we reported the evidence for a photoinduced electron transfer and metastable charge separation in semiconducting polymer/C_{60} composites [3-10]. A schematic description of this phenomenon is displayed in Fig.1.

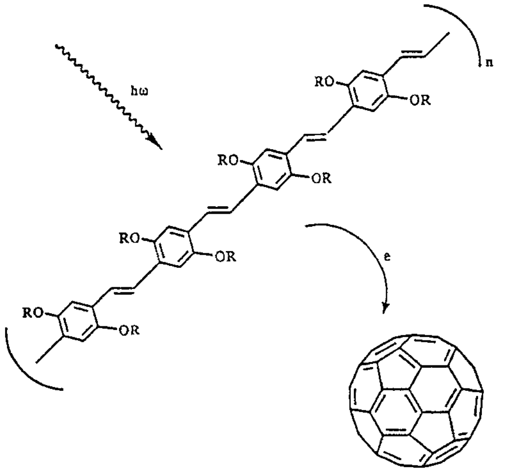

Fig. 1: Schematic representation of the photoinduced electron transfer from conjugated polymers onto C_{60}.

This forward electron transfer from the semiconducting polymer (as donor) onto C_{60} (as acceptor) occurs in less than 1 picosecond, thereby decreasing the luminescence by three orders of magnitude and eliminating intersystem crossing to triplet state. Using this inter-molecular photoinduced charge transfer from donor to acceptor at the interface between a donor-acceptor bilayer consisting of films of the semiconducting polymer, poly(2-methoxy,5-(2'-ethyl-hexoxy)-p-phenylene) vinylene, (hereafter referred to as MEH-PPV) and C_{60}, we were able to fabricate diodes with rectification ratios of approximately 10^4 which operated both as photodiodes and as photovoltaic cells [4].

We review the results of femtosecond time resolved photoinduced absorption, near steady-state photoinduced absorption spectroscopy, steady state light induced electron spin resonance, picosecond transient and steady state photoconductivity, time resolved and cw photoluminescence studies and steady state infrared photoexcitation spectroscopy on semiconducting polymer - C_{60} composites using a series of semiconducting polymers as the donor. In each case, we have investigated the semiconducting polymer alone and in composites with C_{60}. The relaxation of the charge separated state, the temperature dependence of the relaxation, and the dependence on the excitation energy and intensity have been characterized. The results demonstrate ultrafast, sub-picosecond photoinduced electron transfer from semiconducting polymers onto C_{60} and confirm the existence of long-lived charge separated configurations in composites of C_{60} with non-degenerate ground state polymers. In degenerate ground state conjugated polymers, soliton formation, and in polydiacetylenes strongly bound exciton formation, are much faster (and lower energy); thereby inhibiting the electron transfer. This result indirectly supports the effective screening of the Coulomb correlations in conjugated polymers like PPV's exhibiting no detectable hindrance for charge separation.

EXPERIMENTAL

All soluble derivatives of poly (*para*-phenylene)vinylene (PPV) are purchased from UNIAX Corp., Santa Barbara and used without further purification. Synthesis and preparation of highly uniform poly (3-octylthiophenes) (P3OT) are described in early reports [5]. Soluble derivatives of polyacetylene (poly (1,6-heptadiyne), PHDK) are synthesized as described in [11]. C_{60} powder was purchased in high purity (99.99%) from Polygon Enterprises, Texas and later from MER Corp., Tucson, Arizona. Detailed experimental procedures of all the studies are summarized in [10].

RESULTS AND DISCUSSION

Although the time scale for the photoinduced electron transfer can be estimated through the demonstration that the luminescence is quenched by reduction of the associated luminescence decay time, the effect of non-radiative decay channels other than the electron transfer cannot be arbitrarily ruled out. Thus, it is important to observe the electron transfer *directly* by ultrashort time scale spectroscopy. The sub-picosecond photoinduced absorption spectra for P3OT as well as soluble PPV's in their pristine state as well as in composite with C_{60} are displayed in Fig. 2. The effect of C_{60} is clearly observable in the early time spectra in a sub-picosecond time scale. This direct observation clearly demonstrates that the photoinduced electron transfer is indeed ultrafast ($\tau_{ET} < 10^{-12}$ s) in these materials confirming the estimation from the luminescence quenching in our initial reports [3,5]. Furthermore, the femtosecond photoinduced absorption studies show an increase of the lifetimes of the observed charge transferred state with increasing C_{60} concentration in the polymeric host [6].

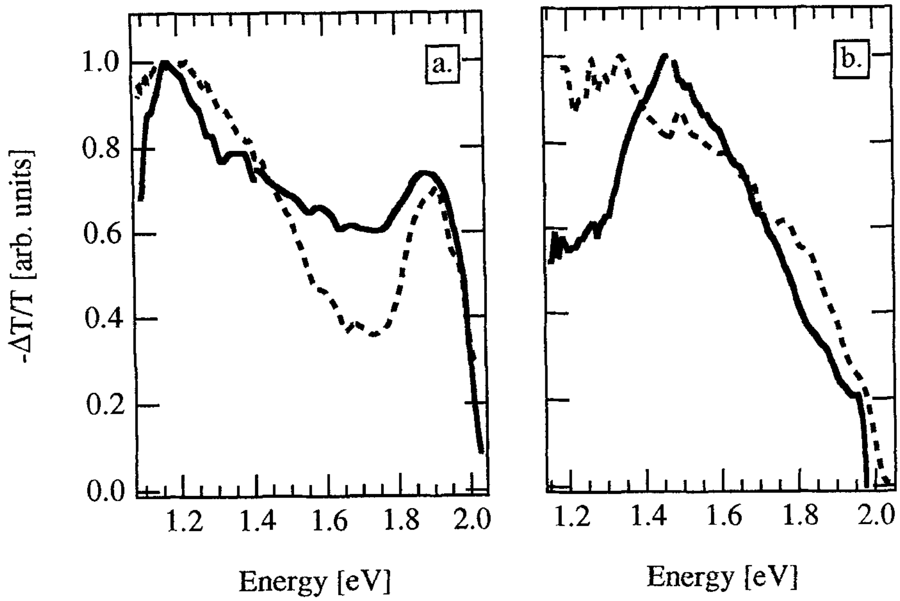

FIGURE 2 a.) Photoinduced changes in the absorption spectrum of P3OT in its pristine state (dashed line) and in composite with 50% C60 (solid line) for 700 fs time delay.

b.) Same for BCHA-PPV in its pristine state (dashed line) and in composite with 1% C_{60} (solid line) for 700 fs time delay.

Changes in the optical absorption spectrum ($-\Delta T/T=\Delta\alpha d$) in the sub-picosecond time scale are in general not related to the observed changes in the millisecond, near steady state time frame; the latter only being sensitive to long-lived photoinduced species like deeply trapped charged excitations or spin forbidden, neutral triplet excitations. The sub-picosecond photoinduced electron transfer, on the other hand, is faster than the inter system crossing as well as the radiative and non-radiative recombination processes as shown above. After the electron transfer, the positive polarons on the polymer host and the negative anion of C_{60} are metastable, creating long-lived charged species. The effect of the photoinduced electron transfer on the millisecond time domain is shown in Fig. 3a. This figure clearly demonstrates the quenching of the triplet-triplet absorption at 1.05 eV creating charged polarons in P3OT [5]. Therefore, it is expected, that the changes in the sub-picosecond photoinduced absorption in the composites should be related to the photoinduced absorption changes in the millisecond time domain as demonstrated in Fig. 3b. Since the absorption spectrum persists without essential change from 5 ps to milliseconds, we conclude that the charge separated state is created at very early times and lives for milliseconds at 80K.

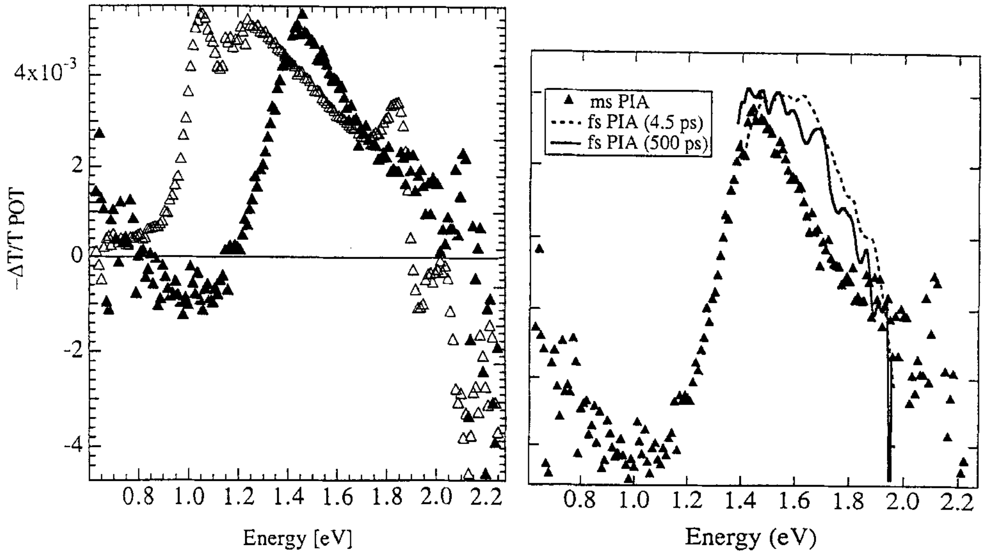

FIGURE 3 a.) Photoinduced absorption spectra of P3OT (open triangles) and P3OT/C60 composite (solid triangles) obtained by pumping with Ar ion laser at 2.41 eV with 50 mW.

b.) Comparison of the early time photoinduced absorption spectra of the P3OT / C60 composite with the near steady state spectrum.

Definitive evidence for a complete electron transfer and a metastable charge separation is obtained from light induced electron spin resonance (LESR) experiments. If the charge separation is long-lived enough (to accumulate the number of spins detectable for the spin resonance within one modulation cycle) there will be two LESR signals observable originating from the positive polaron (donor cation radical) as well as from the anion of the C_{60} (acceptor anion radical). In general, organic radicals have *g*-values around 2.00 which makes it very difficult to distinguish between the donor radical cation and the acceptor radical anion contribution to the LESR signal. Fortunately this is not the case for our semiconducting polymer/C_{60} composites since $C_{60}{}^{-}$ anion radical has an unusually low *g*-value of approximately 1.99 [12] which should give the possibility to distinguish clearly the donor as well as the acceptor contributions to the LESR signal. The results of LESR experiments are displayed in Fig. 4 for two different conjugated polymer/C_{60} composites, comparatively.

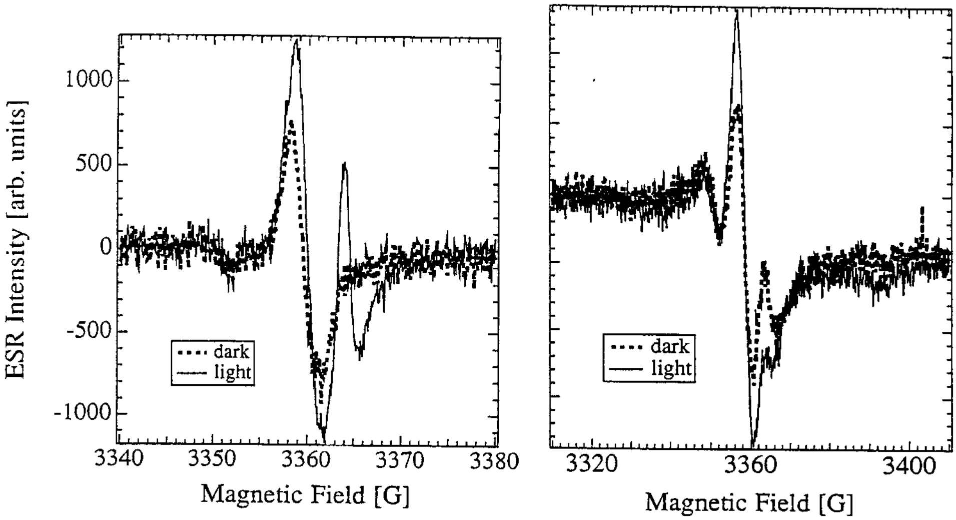

FIGURE 4 LESR spectra of P3OT/C_{60} (a.) and MEH-PPV/C_{60} (b.) composites excited with 514.5 nm Ar ion laser at 80K.

The intensity of the LESR signal decreases upon increasing the temperature following an Arrhenius behaviour (LESR proportional to exp($-E_A$/kT)) with activation energies E_A=15meV as obtained from the fit of the temperature dependent LESR studies as reported earlier [5,10]. The LESR signal is reversible ruling out the permanent photochemical changes in these composites. Furthermore, the intensity of the integrated LESR signal demonstrate that the number of the created cation radicals correspond to the number of the created anion radicals plus an excess of polarons of the polymer photoactivity itself [10].

The ultrafast photoinduced electron transfer from the conjugated polymers onto C_{60} and the following stabilization of the charge separated state should enhance the near steady state photoconductivity of the composites compared to the pure host polymer photoconductivity. This effect is observed to be fairly strong as displayed in Fig. 5 for P3OT/C_{60} as well as MEH-PPV/C_{60} composites [7].

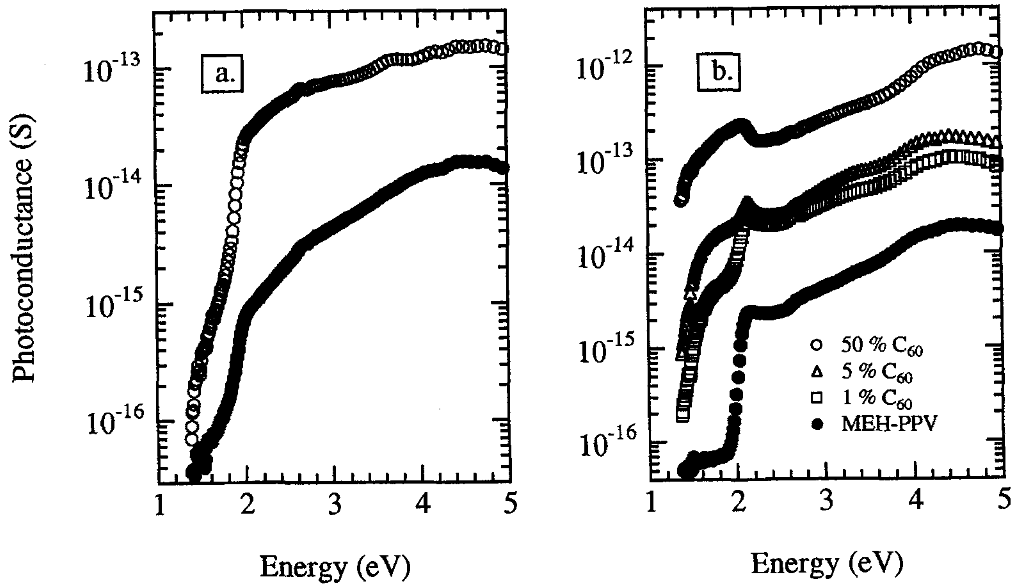

FIGURE 5 a.) Spectral response of the steady state photoconducitivity of a pristine P3OT film (solid circles) and a 5 % P3OT /C_{60} composite film (open circles).

b.) Spectral response of the steady state photoconductivity of MEH-PPV/C_{60} films for various concentrations of C_{60} at room temperature.

It is clearly observable, that addition of only a few percent of C_{60} into the conjugated polymer sensitizes its steady state photocurrent one order of magnitude over the entire spectral range from the near infrared to the ultraviolet. The photocurrent below the absorption edge of the conjugated polymer (around 2 eV) indicates that photoexcitation of C_{60} initiates a photoinduced hole transfer, which is the symmetrical process to the photoinduced electron transfer from the polymer donor. These data have been confirmed by the experiments of Yoshino and coworkers [13,14].

The sensitization of the steady state photoconductivity originates from both of the enhancement of the photoinduced charge carrier generation efficiency as well as the increase in lifetimes of the photoinduced charges. This is demonstrated in Fig. 6 as measured with picosecond transient photoconductivity experiments. This sensitization of the conjugated polymer photoconductivity by C_{60} is effective because the electron transfer rate is ultrafast ($>10^{12}$s); fast enough to be competitive with mechanisms for early time recombination (geminate and/or nongeminate) of photoexcited electrons and holes in the polymer host. Moreover, the lifetime of the transient photoconductivity is extended by the addition of C_{60}, since recombination is inhibited by the spatial separation of the electron and the hole (on the C_{60} acceptor and on the conjugated polymer donor, respectively). This can be visualized as C_{60} being a well defined deep trap for the photoexcited electron, rendering a free hole on the conjugated polymer backbone; *e.g.* photodoping.

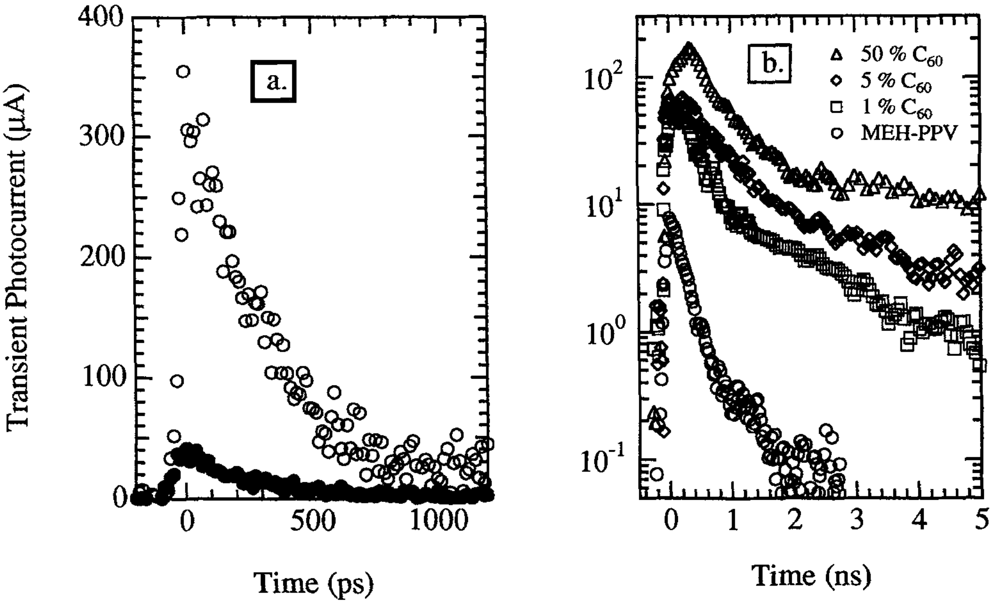

FIGURE 6 a.) Transient photoconducitivity of a pristine P3OT film (solid circles) and a 5 % P3OT /C_{60} composite film (open circles) pumped with 2.9 eVat room temperature.

b.) Transient photoconductivity of MEH-PPV/C_{60} films for various concentrations of C_{60} pumped with 2.9 eV at room temperature.

Another implication of long-lived photoinduced charge separation is the enhancement of the photoinduced infrared vibrational absorption modes (IRAV). These modes originate from the activation of the totally symmetrical Raman modes in the infrared spectrum, due to the strong one dimensional electron phonon coupling in these systems which create local lattice distortions around injected (doping and/or photoexcited) charges. Since the photoinduced electron transfer is responsible for creating long-lived charge carriers (photodoping), this phenomenon is strongly enhanced in conjugated polymer/C_{60} composites as demonstrated in Fig. 7 [8].

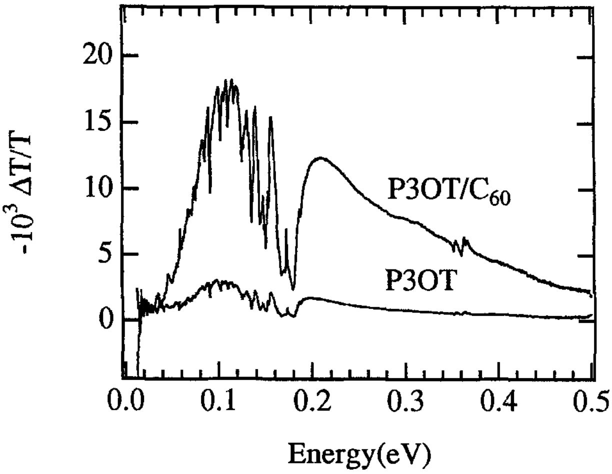

FIGURE 7 Photoinduced infrared absorption spectra of P3OT and P3OT/C_{60} (5%) at 80 K obtained by pumping with Ar ion laser at 2.41 eV with 50 mW/cm^2.

The conditions under which this photoinduced electron transfer is favored are not yet completely clear. The energetics of the donor-acceptor couple are certainly important, as described in Marcus theory [15]. The dielectric constant of the medium also plays an important role. In our comparative studies we observed that degenerate ground state conjugated polymers (PHDK) do not show a photoinduced electron transfer [5]. Recently, we looked at polydiacetylenes (PDA) which also do not show any photoinduced electron transfer onto C_{60}. Studies of picosecond transient photoconductivity, femtosecond photoinduced absorption as well as near steady state photoinduced absorption experiments clearly show that there is no **forward** electron transfer in PHDK/C_{60} and PDA/C_{60} composites, ruling out the possibility of a rapid forward transfer accompanied with a rapid back relaxation. Since the energetics of the PHDK as well as PDA are similar to P3OT (ionization potential, 5.5eV), the striking difference between PPV's (P3OT's) with an ultrafast photoinduced electron transfer, on one hand, and PHDK (PDA's) with complete inhibition of this process, on the other, must have its origin in the photophysics of the conjugated polymer donor itself. The solitonic stabilization deep in the gap for the degenerate ground state polymer is proposed to inhibit the electron transfer process [5]. This limits the forward electron transfer rate to the estimated soliton formation time ($\tau_{ET}>10^{-13}$ s)[5]. For the case of polydiacetylenes we propose that strongly bound (0.5 eV) exciton formation in PDA's inhibits the electron transfer, which requires complete charge separation over the Coulomb barrier. This implies, however, that the Coulomb correlations in PPV's, P3OT's *etc.* are well screened, creating free electron-hole pairs upon photoinduction and no barrier for the rapid electron transfer onto C_{60}[16].

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